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(54) **Forming a thermally black surface on metals**

(57) A stable thermally black layer is formed on molybdenum, nickel, iron, copper, tungsten or an alloy consisting of two or more of these metals by applying a layer from 1 to 10 μm thick consisting of aluminium with or without one of the above-mentioned metals, heating the metal component and superposed layer in an inert atmosphere so as to form a compound of aluminium with one of the said metals, and then partially oxidising the aluminium compound by heating at from 950 to 1200°C in a wet hydrogen atmosphere so that substantially all the aluminium in the aluminium compound is converted into aluminium oxide.

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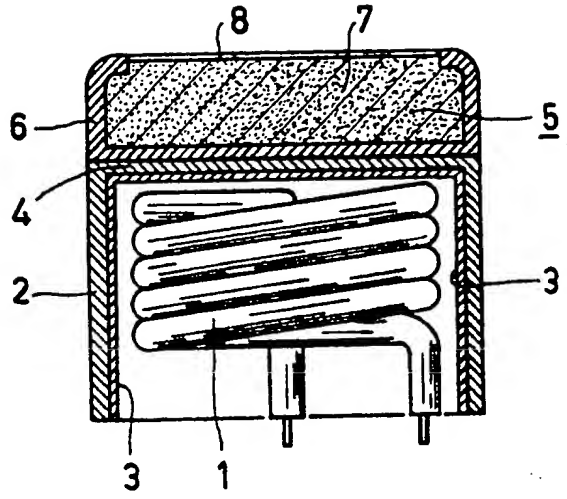
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SPECIFICATION

Method of providing a metal component with a thermally black surface

The invention relates to a method of providing a metal component with a thermally black surface, on which component one or more metals or metal alloys are provided in the form of a layer having a thickness of 1 to 10 μm, which said metals or metal alloys form at least one metal compound with the material of the component or with each other, which metal compound is obtained by heating in a substantially non-reactive atmosphere.

The invention also relates to a method of providing a deep-drawn cathode shaft at least on its inside with a thermally black surface.

It is generally known that the capacity of metals of taking up and radiating thermal energy can be augmented by providing them with a thermally black surface. For example, a shadow mask in a colour display tube is blackened so as to increase the heat-radiating capacity. It is also known in cathode shafts to thermally blacken the inner surface and/or the outer surface so as to obtain in this manner an indirectly heated cathode having a short warming-up time.

Such a method described in the opening paragraph is disclosed in German Patent Specification 868,026. In this Specification a method is described of providing metals with a thermally black surface, in which a thin, for example approximately 10 μm thick layer of aluminium or a layer of an aluminium alloy is provided on molybdenum. By heating in a non-reactive atmosphere, a rough surface layer of a metal compound consisting of aluminium and molybdenum is formed. The disadvantage of such a thermally black layer consisting, for example of Al_3Mo is that the aluminium evaporates from the compound at higher temperatures (800 to 1200°C), resulting in the layer becoming less black. However, when such black surface coatings are used in electron tubes, display tubes and camera tubes, the evaporated aluminium forms a metal mirror elsewhere in the tube, which is not desired.

It is therefore an object of the invention to provide a method of forming a thermally black surface on a metal component, which thermally black surface can withstand high temperatures (800 to 1200°C) and a high thermal load.

Another object of the invention is to provide a method of forming a thermally black surface at least on the inside surface of deep-drawn cathode shafts.

The invention provides a method of forming a superficially thermally black layer on a surface of a metal component, wherein at least the surface of the metal component consists of molybdenum, nickel, iron, tungsten, copper or an alloy consisting of two or more of these metals, the method nickel, iron, tungsten or copper, heating the metal component and superposed layer so as to form an aluminium compound with one of the metals molybdenum, nickel, iron, tungsten or copper, this heating step being performed in an atmosphere which does not react substantially with aluminium or any of the said metals, and then partially oxidising the aluminium compound by heating at from 950 to 1200°C in a wet hydrogen atmosphere so that substantially all the aluminium in the aluminium compound is converted into aluminium oxide and a superficially thermally black layer is produced. This thermally black layer remains thermally black after heating to a high temperature, for example, 1200°C, and can withstand high thermal loading. The provided layer may consist exclusively of aluminium. However, it is alternatively possible to provide a layer consisting of, for example, aluminium and molybdenum, preferably in a molecular ratio 3Al:1Mo so that the formation of the aluminium compound Al_3Mo occurs more easily. The provision of the aluminium and possibly the other metals can be done by means of electrolysis, cataphoresis, vapour-deposition or sputtering, or by providing a layer of a suspension with aluminium powder mixed, if desired, with powder of one of the above specified metals.

In indirectly heated cathodes, a filament is present in a cathode shaft to which or in which an emissive member is fixed. When the inner surface of the cathode shaft is thermally black, this surface absorbs heat emitted from the filament quickly and effectively. If the outside of the cathode shaft also bears a thermally black surface, much heat will be radiated from the cathode shaft at high temperatures, so that a comparatively large heating energy input is required to maintain the cathode at the emission temperature. However, this large heating energy input ensures a short warming-up time of the cathode. It has hitherto proved difficult to provide deep-drawn cathode shafts on the inside with a very smooth thermally black layer which can withstand high temperatures (for example, 1,000°C).

According to the invention it is possible to manufacture deep-drawn cathode shafts which are coated on at least the inside with a thermally black layer which is from 1 to 10 μm thick, and which contains Al_2O_3 and can withstand high temperatures, by means of a method in which a foil is used which consists at least on one surface of one or more of the metals Mo, Ni, Fe, W or Cu, or an alloy which consists of two or more of these metals, which metal or alloy is coated with a thin layer of aluminium or a layer consisting substantially of aluminium, which is converted into the aluminium compound cathode shafts are then manufactured from the plate thus coated by means of a deep-drawing process, after which the firing tr atment in wet hydrogen takes place.

By performing the deep-drawing process prior

obtained. The aluminium layer in that case may not be more than 4 to 5 μm thick, since the cathode shaft material cannot be deep-drawn when the black layer is too thick. The minimum layer thickness must be 1 μm so as to be able to obtain a continuous black layer. The metal component consists at least at its surface of one of the above-specified metals or of an alloy consisting of two or more of the above-specified metals. So the component may be, for example, a nickel-coated iron cathode shaft or another component from stratified material or an alloy, for example, a nickel-iron alloy, or a copper-nickel alloy. The invention will now be described in greater detail with reference to a few examples.

EXAMPLE 1

A 2 μm thick layer of aluminium was vapour deposited on one side of a 100 μm thick molybdenum foil. The coated foil was then heated to 800°C in an oxygen-free atmosphere, for example, in a vacuum or in a protective gas, for example, dry hydrogen. The aluminium layer reacted with the molybdenum forming a black layer containing Al_3Mo. This foil was then used as a starting material for the manufacture of deep-drawn cathode shafts, the thermally black surface being disposed on the inside. The cathode shafts thus manufactured were then fired in wet hydrogen at 1,000°C (dew-point 0°C to 20°C). The minimum required temperature was 950°C. As a result of this firing process, the aluminium from the aluminium-molybdenum compound was converted into aluminium oxide, so that inside the cathode shaft a thermally black smooth, aluminium oxide-containing surface was produced which could withstand high temperatures (800 to 1200°C).

EXAMPLE 2

A mild steel shadow mask was dipped in a suspension containing particles (less than 1 μm in diameter) of aluminium in *n*-butyl acetate, an approximately 2 μm thick aluminium layer being deposited on the shadow mask. After drying, the coated mask was heated to 750°C in dry hydrogen. The aluminium layer reacted with the iron and formed a thermally black layer. The shadow mask is then fired in wet hydrogen at 1,100°C, so that the aluminium in the aluminium-iron compound was oxidized and a resistant thermally black surface was obtained.

EXAMPLE 3

A copper cooling plate was provided with a 5 μm thick layer consisting of aluminium and copper by means of a sputtering process, and was then heated to approximately 800°C in a non-reactive atmosphere. The cooling plate was then fired in wet hydrogen at 1,000°C. The cooling plate thus treated did not appear black but was more or less yellow. This yellow surface coating

EXAMPLE 4

An approximately 2 μm thick layer of aluminium was vapour-deposited onto a mild steel shadow mask which is provided with a 10 μm thick layer of nickel — and the mask was then heated in a vacuum (13μ Pa) up to approximately 800°C. The aluminium layer reacted with the nickel and formed a thermally black layer. The shadow mask was then fired in wet hydrogen at approximately 1,100C, the aluminium in the aluminium-nickel compound being oxidized and a thermally black surface which can withstand high temperatures being obtained.

EXAMPLE 5

A grid wound from wire for an electron tube consisting of an iron-nickel alloy, FeNi (50/50) was provided by vapour-deposition with a 2 μm thick layer of aluminium, and was then heated in a vacuum up to approximately 800°C. The grid was then fired in wet hydrogen at approximately 1,000°C, the grid obtaining a thermally black very resistant surface.

A cathode including a cathode shaft having a thermally black layer produced on its inside surface by a method according to the invention will now be described with reference to a drawing, the single Figure of which shows a cathode having a cathode shaft and a thermally black surface on the inside surface of the cathode shaft. A filament 1 is located within a cavity defined by a deep-drawn molybdenum cathode shaft 2, which cathode shaft 2 has a wall thicknes of 0.05 mm. By means of a method according to the invention, the inside surface of the cathode shaft 2 was coated with a thermally black Al_2O_3-containing layer 3 approximately 3 μm thick, so that the thermal energy radiated by the filament 1 could be absorbed rapidly and effectively. An emissive member 5 consisting of a holder 6 with therein a tungsten member 7 impregnated with emissive material was secured to the end face of the cathode shaft 2. The surface 8 forms the emissive surface of the cathode.

CLAIMS

1. A method of forming a superficially thermally black layer on a surface of a metal component, wherein at least the surface of the metal component consists of molybdenum, nickel, iron, tungsten, copper or an alloy consisting of two or more of these metals, the method comprising the steps of applying a layer from 1 to 10 μm thick layer consisting of aluminium or of aluminium and one of the metals molybdenum, nickel, iron, tungsten or copper, heating the metal component and superposed layer so as to form an aluminium compound with one of the metals molybdenum, nickel, iron, tungsten or copper, this heating step being performed in an atmosphere which does not react substantially with aluminium or any of the said metals, and then partially oxidising the aluminium compound by heating at from 950 to 1200°C in a wet hydrogen atmosphere so that

compound is converted into aluminium oxide and a superficially thermally black layer is produced.

2. A method of forming a superficially thermally black layer on a surface of a metal component, substantially as herein described with reference to any of Examples 1 to 5.

3. A method of providing a deep-drawn cathode shaft at least on its inside surface with a thermally black surface by means of the method as claimed in Claim 1, characterised in that a plate is used which consists at least on one surface of a metal from the said group of metals or an alloy which contains at least one metal from the said group of metals, which metal or alloy is coated with a thin layer of aluminium or a layer consisting substantially of aluminium, which is converted into the aluminium compound, cathode shafts are then manufactured from the plate thus coated by means of a deep-drawing process, after which the firing treatment in wet hydrogen takes place.

4. A cathode comprising a metal cathode shaft coated at least on its inside surface with a thermally black layer produced by means of a method as claimed in Claim 3.

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